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Structure, Strength and Conductive Properties of Vacuum Cu-Ta Condensates

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Structure, strength and electrical conductivity of Cu-Ta vacuum condensates with a tantalum concentration from 0.1 to 3 at % is studied. Depending on the content of tantalum, the condensates have different structural states: one- and two-phase, supersaturated tantalum solution in FCC copper lattice. Alloying of copper condensates with tantalum reduces the grain size from ~ 3 μm to ~ 50 nm. The optimum ratio of strength properties and electrical conductivity is realized at a tantalum content of ~ 0.4 – 0.5 at. %. In this case, the ultimate tensile strength reaches ~ 1000 MPa with an electrical conductivity of ~ 50 % of the single-component copper. It is shown that the main contribution to the increase in strength is made by grain boundary strengthening due to the decrease in the grain size and the increase in the Hall-Petch constant.

Keywords: Grain size, Grain boundary segregation, Strength, Hardness, Conductivity.

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1. INTRODUCTION

A feature of the Cu-Ta system is the very low (at the level of detectability) mutual solubility between the components and the absence of chemical compounds under equilibrium conditions in both solid and liquid states. The boiling point of copper, which is 2560 °C, is less than the melting point of tantalum – 2980 °C [1]. This circumstance does not allow obtaining alloys of copper and tantalum with melting and casting technologies. They are synthesized mainly by powder and vacuum-plasma methods, realizing a wide range of structural states: from anomalous oversaturated solid solutions to heterogeneous systems with a micro- and nanometer dimension. These objects demonstrate high mechanical properties [2] and thermal stability of the initial nanoscale grain structure [3, 4]. It should be noted that most of the research is devoted to materials that are obtained by powder methods [2 3, 5]. There is practically no information about the strength and electrophysical properties of films, foils and coatings obtained by vacuum-plasma technologies and the relationship of these properties with the structure [6, 7]. In this connection, the aim of this paper was to study the structure, strength and electrical conductivity of Cu-Ta condensates foils obtained by evaporation-condensation of constituent components in a vacuum (PVD technology).

2. EXPERIMENTAL

The objects of research were foils of one-component copper condensates and two-component Cu-Ta 40-50 μm thick obtained by electron beam evaporation from various sources and subsequent crystallization on non-orienting glass ceramic substrates in vacuum at a pressure of ~ 10^{-3} Pa.

The structure of condensates was studied by transmission electron microscopy using PEM-100, JEM-2100 instruments and by X-ray diffractometry on a DRON-3M apparatus.

The integral content of tantalum was determined by X-ray fluorescence analysis.

The local concentration of tantalum was determined by energy dispersive X-ray spectroscopy (EDS).

The mechanical properties were studied in the active stretching regime on a TIRATEST-2300 apparatus, the microhardness was measured on a PMT-3 instrument. The electrical resistivity was measured by a compensation method [8].

3. EXPERIMENTAL RESULTS

Fig. 1 shows the concentration dependences of the grain size (L) and the period of the crystal lattice (a) of the copper matrix on the tantalum content for vacuum condensates obtained under the same process conditions. It can be seen that for small tantalum contents up to ~ 0.3-0.4 at. %, there is a sharp decrease in the value of L from 1.3 μm to 50 nm.

It is important to note that at such concentrations of tantalum there is no noticeable change in the period of the FCC copper crystal lattice (Fig. 1, curve 2). On the electron diffraction patterns of the samples corresponding to the descending branch of the $L-f$ (at. % Ta) dependence, diffraction reflexes belonging only to copper was detected. On the bright-field and dark-field images there are no signs that indicate the presence of a second phase in the condensate volume (Fig. 2). Further increase in the concentration of tantalum in the condensates leads to an increase in the lattice period of copper, which indicates the formation of a supersaturated solid solution of tantalum in the FCC copper crystalline lattice. Additionally, the appearance of tantalum particles in the volume of a copper matrix is indicated by diffraction reflections belonging to BCC and FCC Ta on electron diffraction patterns (Fig. 3). The grain size remains practically constant throughout the concentration interval.

Thus, the above results allow us to conclude that with a tantalum content of ~ 0.3-0.4 at. %, it has a

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modifying effect on copper condensates, concentrating on the boundaries of the copper matrix metal grains, blocking their growth upon the deposition of a two-component metallic vapor. At a higher concentration of tantalum, a supersaturated solution forms in the copper lattice and the formation of particles of the second phase in the volume of the copper matrix takes place. A similar phenomenon was observed in two-component Cu-Mo, Cu-Co [6], Fe-W [7], Al-Fe [9] condensates.

Fig. 4, 5, and 6 show the results of studies of the strength properties of condensates on the tantalum concentration. All the experimental curves have two sections: with a tantalum content of up to about 0.4 at. %, a sharp increase in all strength characteristics and a decrease in deformation before fracture are observed. The specific electrical resistance in this range of concentrations varies insignificantly (Fig. 6). A further increase in tantalum content leads to a decrease in the intensity of growth of strength and reduction of deformation to failure. On the contrary, the resistivity increases substantially.

The processing of experimental data on the physical yield stress in the $\sigma - f\ (L^{-1/2})$ coordinates indicates an increase in the Hall-Petch constant from $0.11\ \mathrm{MPa \cdot m^{-1/2}}$ to $0.37\ \mathrm{MPa \cdot m^{-1/2}}$ for one-component copper and two-component Cu-Ta condensates, respectively (Fig. 7). Note that the Hall-Petch dependence was built for samples with a tantalum content corresponding to the descending branch of the $L - f$ (at. % Ta) dependence (Fig. 1). A comparison of the strength properties of condensates studied in this paper with the results of [5], in which Cu-Ta alloys obtained by powder technologies were studied, is shown in Fig. 7. It can be seen that the achieved level of strength at comparable concentrations is approximately the same.

Fig. 8 shows the results illustrating the combination of strength properties and resistivity for various copper-based alloys. It follows from the presented data, that Cu-Ta condensates have strength properties at the level of belillium bronzes, exceeding them in electrical conductivity.

4. RESULT AND DISCUSSION

The presented results indicate different mechanisms of strengthening of condensates with tantalum contents corresponding to increasing and gently sloping regions of concentration dependences of strength properties (Fig. 4, 5). Indeed, a comparison of the concentration dependences of the grain size and the period of the crystal lattice of the copper matrix with strength properties indicates a certain correlation between them. First of all, attention is drawn to the equality of tantalum concentrations at which changes in the character of all the experimental dependences of both structural parameters and various properties occur. This tantalum content of ~ 0.4 at. %, as shown in [4], is necessary and sufficient to form segregations of tantalum atoms in the form of monoatomic adsorption layers at the grain boundaries of the copper matrix. In this state of grain-boundary segregations, strong interatomic bonds between tantalum and copper atoms are realized, which increase the cohesive strength of the grain boundaries. Indeed, as follows from Fig. 4, 5, 6, the maximum strength properties are achieved with a tantalum content of about 0.4 at. %. At this concentration, there is no appreciable solubility of the tantalum atoms in the crystal lattice of copper (Fig. 1), and accordingly there is no strong increase in the resistivity (Fig. 6). In the structure of the condensates there is no noticeable number of particles of the second phase, which minimizes the dispersion hardening. But at this concentration, the maximum reduction in the grain size of the copper matrix occurs, and grain boundary strengthening involves two factors. First, the increase in strength properties is due to the reduction in the grain size of the copper matrix, secondly, due to the increase in the Hall-Petch coefficient (Fig. 7) [6].

Thus, our study reveals that the optimal structural state of the objects is that at which the tantalum atoms are in the grain boundaries in the form of equilibrium grain boundary segregation, which are monatomic adsorption layers. In this case, high strength and electrically conductive properties of condensates are realized in the initial state. With a further increase in the concentration of tantalum, there is an insignificant increase in the strength properties and a significant increase in the resistivity (Fig. 4, 6) due to the formation of anomalous supersaturated tantalum solutions in the FCC crystal lattice of copper (Fig. 1).

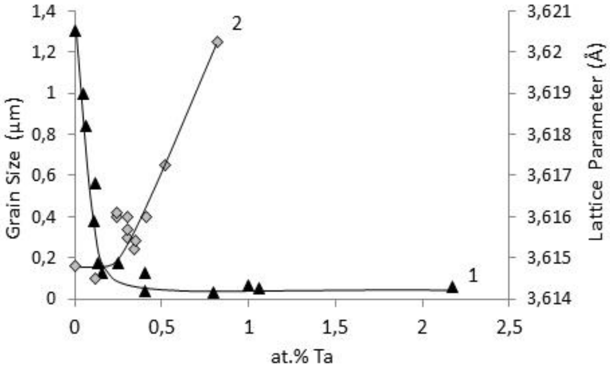
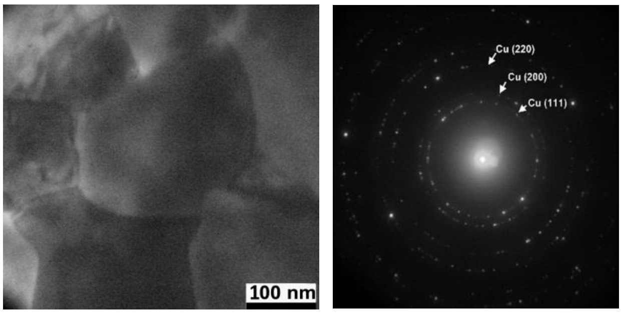
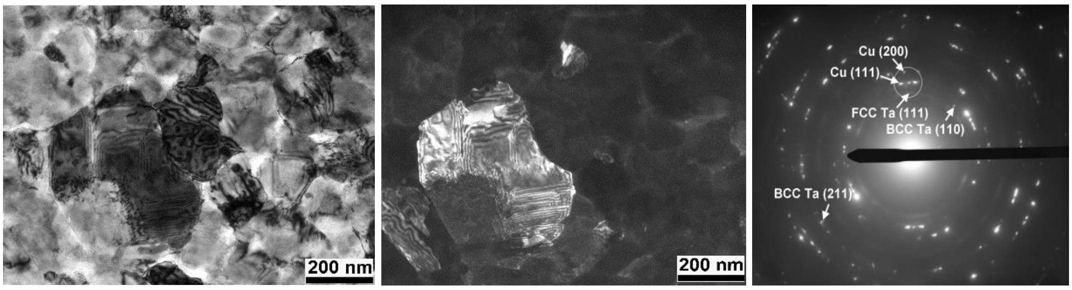


Fig. 1 – Concentration dependences of the grain size (1) and the lattice period (2) of Cu-Ta vacuum condensates



a b

Fig. 2 – Electron-microscopic images of the structure of Cu-0.15 at. % Ta condensates: a) bright-field image, b) electron diffraction pattern



a b c

Fig. 3 – Electron microscopic images of the structure of Cu-1.3 at. % Ta condensates: a) bright-field image, b) dark-field image, c) electron diffraction pattern

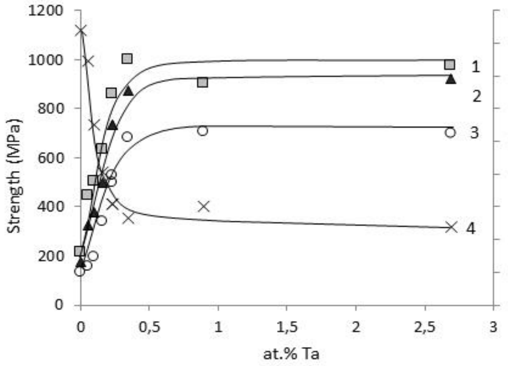


Fig. 4 – Concentration dependences of the strength properties of Cu-Ta vacuum condensates: 1 – ultimate strength, 2 – conventional yield strength, 3 – physical yield strength, 4 – deformation before failure

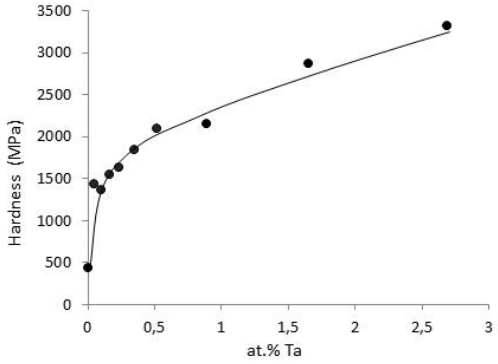


Fig. 5 – Dependence of microhardness of Cu-Ta vacuum condensates on tantalum concentration

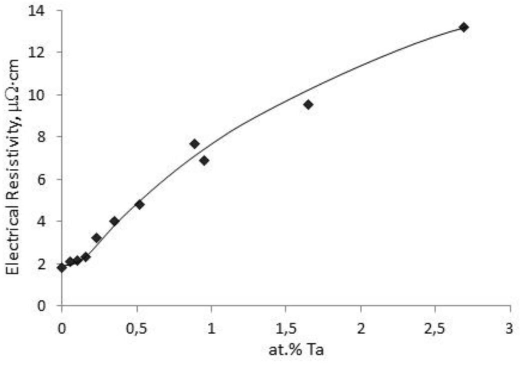


Fig. 6 – Effect of tantalum on the electrical resistivity of Cu-Ta vacuum condensates

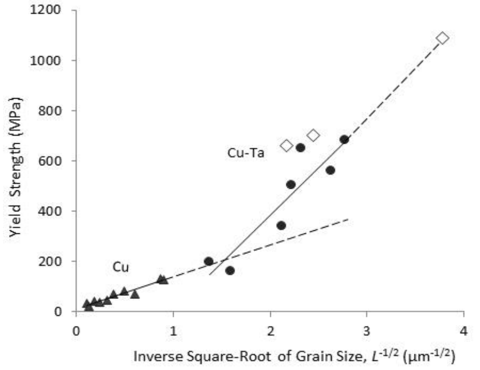


Fig. 7 – Hall-Petch dependences: ▲ – copper vacuum condensates, ● – Cu-Ta vacuum condensates, ◇ – Cu-Ta alloys studied in [5]

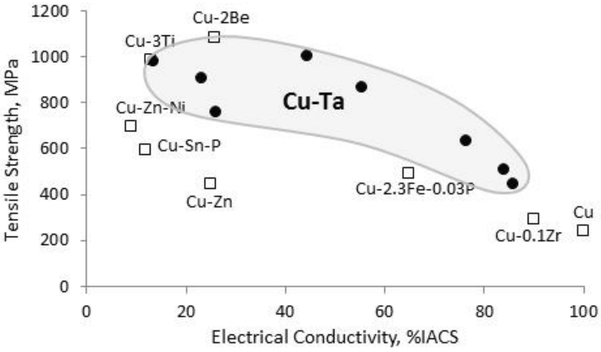


Fig. 8 – Strength and electrical conductivity of copper-based alloys: □ – [10], ● – Cu-Ta alloys studied in this paper

5. CONCLUSIONS

1. The structure, strength and electrical conductivity of Cu-Ta vacuum condensates in the range of tantalum concentrations of 0.1-3 at. % are studied.

2. It is established that tantalum has a modifying effect on copper condensates, increasing their strength properties and dispersing the grain structure up to the nanoscale dimension.

3. It is shown that the optimal combination of strength properties and electrical conductivity have condensates containing 0.4 at. % Ta. In this case, the tensile strength reaches ~ 1000 MPa with an electrical conductivity of ~ 50 % of the single-component copper.

4. The main contribution to the achieved level of

strength is made by grain-boundary strenthening, which is caused both by a reduction in the grain size of the copper matrix and by an increase in the Hall-Petch constant. The observed regularities are explained by the formation of segregation at the grain boundaries of the copper matrix by tantalum atoms in the form of monoatomic adsorption layers.

Структура, міцнісні та електропровідні властивості вакуумних конденсатів Cu-Ta

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Вивчено структуру, міцнісні та електропровідні властивості вакуумних конденсатів Cu-Ta з концентрацією танталу від 0.1 до 3 ат. %. Залежно від вмісту танталу об'єкти дослідження мають різний структурний стан: одно- і двофазний, пересичений розчин танталу в ГЦК рещітці міді. Легування конденсатів міді танталом знижує величину зерна від ~ 3 мкм до ~ 50 нм. Оптимальне співвідношення міцнісних властивостей і електропровідності реалізується при вмісті танталу ~ 0.4-0.5 ат. %. При цьому межа міцності сягає ~ 1000 МПа при електропровідності ~ 50 % від однокомпонентної міді. Показано, що основний внесок в збільшення міцності вносить зернограничне зміцнення через зменшення величини зерна і підвищення коефіцієнта Холла-Петча.

Ключові слова: Розмір зерна, Зернограничні сегрегації, Міцність, Твердість, Електропровідність.

Структура, прочностные и электропроводящие свойства вакуумных конденсатов Cu-Ta

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Изучены структура, прочностные и электропроводящие свойства вакуумных конденсатов Cu-Ta с концентрацией тантала от 0.1 до 3 ат. %. В зависимости от содержания тантала вакуумные конденсаты имеют различное структурное состояние: одно- и двухфазное, пересыщенный раствор тантала в ГЦК решетке меди. При легировании конденсатов меди танталом удается снизить величину зерна от ~ 1.3 мкм до ~ 50 нм. Оптимальное сочетание прочностных свойств и электропроводности реализуется при содержании тантала ~ 0.4-0.5 ат. %. При этом предел прочности достигает ~ 1000 МПа при электропроводности составляющей ~ 50 % от однокомпонентной меди. Показано, что основной вклад в увеличении прочности вносит зернограничное упрочнение из-за уменьшения величины зерна и повышения коэффициента Холла-Петча.

Ключевые слова: Размер зерна, Зернограничные сегрегации, Прочность, Твердость, Электропроводность.

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